

Hot-electron femtochemistry at surfaces: on the role of multiple electron processes in desorption

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Abstract

Aspects of molecular processes at surfaces due to sub-ps laser pulses of visible light are discussed here. Within the limits of the standard two-temperature model describing the temporal evolution of fs laser-excited substrate electrons, a theoretical contribution to our understanding of desorption induced by fs laser stimulation is presented which includes, in a rudimentary way, multiple inelastic hot-electron scattering from the adsorbate. Results of the present model suggest that the degree of electron multiplicity (significantly less than 10) in fs-laser-induced-desorption is not as great as implied by previous DIMET (= desorption induced by multiple electronic transitions) or stochastic friction models. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Hot-electron-induced molecular processes at surfaces have provided the fundamental basis for what is increasingly referred to as surface femtochemistry (SF) [1–4]. First realizations of SF followed the script in which sub-nanosecond, pulsed visible laser light was directed upon an adsorbate (usually NO, O₂, or NH₃)-covered metal surface resulting in some chemical transformation involving the adsorbed molecules. The initial ‘elementary reaction’ observed and reported was desorption, the breaking of the substrate–adsorbate bond. Experimentally, in addition to choice of systems to be investigated, one could vary the incident photon wavelength, angle-of-incidence, polarization, intensity and the temporal structure of the pulses (e.g. pulse widths, rise times,

rep rates, etc.). Measured attributes included state-specific rates and/or yields, not only the dependence on final electronic state but also on the final translational energy, direction, and internal vibrational and rotational states. Pioneering work in laser induced SF has occurred in several laboratories [5–20]. This work and modern surface photochemistry in general have been the focus of many excellent and comprehensive reviews [1–4,21–24] which provide background for the contributions in this dedicated volume.

The mechanistic picture that has emerged from these studies is some variation on the following theme. The incident photon pulse creates a non-equilibrium continuous distribution of hot electrons with energies in the range $\epsilon_{\text{Fermi}} < \epsilon_{\text{in}} \leq \epsilon_{\text{Fermi}} + h\nu$ where ϵ_{Fermi} is the Fermi level of the substrate and $h\nu$ the photon energy, as illustrated in Fig. 1a. This results in a transient flux of hot electrons incident upon the surface from within. Subsequent inelastic

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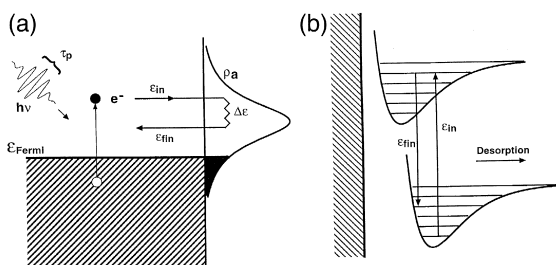


Fig. 1. Energy diagrams for inelastic hot electron scattering. (a) Electronic energy levels showing photon creation of conduction band electron-hole pair and subsequent inelastic scattering through adsorbate resonance characterized by ρ_a , the local density of states. (b) Adsorbate-substrate potential energy curves for electronic ground (bottom) and temporary negative ion resonance (top) states.

scattering of these hot electrons by the adsorbed molecules possibly [25–30], but not exclusively [31,32] via a temporary negative ion shape resonance provides a mechanism for redistributing energy from the hot electrons into the various motional degrees of freedom of the molecules. As depicted in Fig. 1b, if the energy placed into center-of-mass translations exceeds the relevant bond energy, then desorption far beyond that expected from thermal laser heating may occur. Theoretical modeling, at various levels of complexity, has provided both a conceptual and at least semi-quantitative degree of understanding to this picture [33–59] and Chapter 19 in [22]. The unresolved theoretical issues can be placed into a number of specialized sub areas such as:

- (i) ground and excited potential energy surfaces;
- (ii) many-degree-of-freedom quantum, semi classical, or classical dynamics, as appropriate;
- (iii) non-adiabatic dynamics associated with the continua of substrate excited states;
- (iv) transient relaxation dynamics and non-equilibrium statistical mechanics.

The work discussed here will be concerned with some implications of the transient hot electron energy distributions produced by the pulsed laser excitation, dealing mainly with issues in categories (iii) and (iv) above.

Experiments have demonstrated that with respect to fluence (= total energy content per unit area)-dependencies, there are at least two unique regimes of hot electron induced desorption: one in which the

desorption yields are directly proportional to the fluence of the incident pulse [5,6]; and the other in which the yields vary as some higher (usually non-integer) power of the fluence [7–11]. Current wisdom has it that within the linear regime desorption is due to a single inelastic scattering event with an unrelaxed ballistic hot electron. This is often referred to as DIET (= desorption induced by electron transitions) [2–4,22–24,32–48]. In contrast, desorption within the non-linear regime has been attributed to multiple excitation events, either as an m -fold generalization of DIET, called DIMET (m = multiple) [7–9,39,40,48] or as an electronic-friction-driven stochastic process [48,60–64]. One of the defining characteristics of both the DIMET and friction pictures is that a ‘large’ number of ‘hits’, either explicitly from hot electrons or implicitly from an effective stochastic force are involved. While the DIMET picture/simulations presented by the IBM group [39,40,48], Chap. 19 in [22] suggest that $m > 10$, both Saalfrank and Kosloff [46] and also Guo [43] have offered DIMET models in which the multiplicity is estimated to be in the range ~ 2 –8 or so. A major intent of the present paper is to further examine this unresolved aspect of elementary surface femtochemistry. Expectations inspired by the long-standing Richardson–Dushman model for thermionic electron emission [65,66] will be outlined and ultimate limits to hot electron SF will be discussed. Significant insights have been drawn from considerations of related phenomena in which hot electron currents are produced by tunnel junctions [36,67], electrochemical cells [68,69], and STM’s (as inelastic tunneling paradigms [70–77], as single atom/molecule switches [78–82], and as ‘angstrochemistry’ protocols [83,84]).

The outline of this paper is as follows. The conceptual background required to deal with resonant inelastic electron scattering from molecules adsorbed on surfaces will be presented in Section 2. The so-called ‘two (or more!) temperature model’ for characterizing transient laser excitation and subsequent equilibration/relaxation at surfaces will be introduced. Implications with respect to the consequent hot electron production will be considered along the lines of the Richardson equation for thermionic emission from the bosonized (= electron-hole pairs) electron gas. Section 3 deals

with multiple-step excitation, particularly in relation to single step processes such as DIET. Numerical consequences are presented in Section 4 and a final summary in Section 5.

2. Background

Here we sketch out, in the simplest way possible, some crucial ingredients in a scattering approach to DIET/DIMET. Attention is focused on those aspects that determine the most likely degrees of multiplicity, given a specified initial laser excitation pulse and hence, via the multiple-temperature model [7,39,48,85–91], see also Chapters 14, 19 and 20 in [22], a consequential time-dependence for the hot-electron temperature.

2.1. DIET

Current theories of DIET, that is single electron desorption, have shown that the desorption (or bound-to-continuum transition) rate is related to the cross section for inelastically scattering hot electrons, initially with energy ε_{in} to $\varepsilon_{\text{in}} - \Delta\varepsilon$, where $\Delta\varepsilon$ is the energy loss into adsorbate excitations (most importantly center-of-mass motion associated with the bond to be broken). This transition rate $\equiv \Gamma_0$ is expressed as the product of $\sigma_{\text{Tot}}(\varepsilon_{\text{in}}, \Delta\varepsilon)$, the total inelastic cross section, multiplied by $j'_{\text{el}}(\varepsilon_{\text{in}})$, the (directionally randomized) distribution of the energetically viable hot electron flux incident upon the adsorbed molecule, integrated over the entire range of incident energy and over those energy losses in excess of D , the desorption energy; that is:

$$\Gamma_0 \approx \int_D^{\varepsilon_{\text{max}}} d\Delta\varepsilon \int_{\varepsilon_{\text{min}}}^{\varepsilon_{\text{max}}} d\varepsilon_{\text{in}} j'_{\text{el}}(\varepsilon_{\text{in}}) \sigma_{\text{Tot}}(\varepsilon_{\text{in}}, \Delta\varepsilon; \tau_R) \quad (1)$$

where τ_R is the lifetime of the negative ion resonance state. In the case of $(h\nu)$ photon-excited electrons, at zero temperature the limits $\varepsilon_{\text{max}} = \varepsilon_{\text{Fermi}} + h\nu$ and $\varepsilon_{\text{min}} = \varepsilon_{\text{Fermi}} + \Delta\varepsilon$ properly account for energy conservation and phase space blocking imposed by the Pauli exclusion principle. Within a Born–Oppenheimer separation of electronic and nuclear exci-

tation, the total resonance cross section can be written as:

$$\sigma_{\text{Tot}}(\varepsilon_{\text{in}}, \Delta\varepsilon; \tau_R) \approx \sigma_{\text{el}}(\varepsilon_{\text{in}}, \Delta\varepsilon; \Delta_0 = \hbar/\tau_R) P(\Delta\varepsilon; \tau_R) \quad (2)$$

where σ_{el} is the energy-normalized electron capture/scattering cross section evaluated at some appropriate fixed molecular geometry and $P(\Delta\varepsilon)$ is the probability per scattering event that center-of-mass nuclear motion becomes excited by the energy increment $\Delta\varepsilon$ lost by the electron. While the fact that both σ_{el} and $P(\Delta\varepsilon)$ depend upon τ_R has been explicitly noted in Eqs. (1) and (2), this parametric dependence will henceforth only be implied. For present purposes the energy dependence of σ_{el} is an unessential detail, so for simplicity it will be replaced by some constant effective value. Thus the electron scattering rate which follows from Eqs. (1) and (2) reduces to:

$$\Gamma_0 \approx j_{\text{el}}(D) \langle \sigma_{\text{el}} \rangle p(\Delta\varepsilon \geq D) \quad (3)$$

where $j_{\text{el}}(D)$ is the total incident flux in which a single electron has energy in excess of D , that amount required to break the bond and $p(D) \equiv \int_D^{\varepsilon_{\text{max}}} P(\Delta\varepsilon) d\Delta\varepsilon$ is the total probability per encounter that the requisite bond-breaking energy has been delivered into nuclear motion within the bond [33,35,36].

The overall rate of desorption is typically obtained from the master equation for the time-dependent probability distribution for the occupation of vibrational and continuum states associated with the bond [39,49–51,75–77,92–98]. Frequently the solution of the master equation reveals the existence of a rate-limiting bottleneck state such that the overall rate is simply:

$$dN/dt \equiv R(t) = p_{\text{BN}} \times \Gamma_{\text{BN} \rightarrow \text{final}} \quad (4)$$

where p_{BN} is the occupation probability for the ‘bottleneck’ and $\Gamma_{\text{BN} \rightarrow \text{final}}$ is the (inelastic electron scattering) rate for the final process, that one in which the adsorbate is excited from the bottleneck to a continuum desorptive state. For low temperature DIET, the ‘bottleneck’ is identically the initial vibrational ground state, hence $p_{\text{BN}} = 1$, $\Gamma_{\text{BN} \rightarrow \text{final}} = \Gamma_0$, and trivially, $R(t) = \Gamma_0$. The atomic-level-basis for this limit has been discussed in detail elsewhere [33–38].

2.2. Two-temperature model

A considerable body of ultrafast-laser-excited-phenomenology has been analyzed in terms of the two (or more) temperature model [22,85–91]. The essential feature is that a temporally narrow incident laser pulse first excites (or super-heats) the near-surface conduction band electrons and then these excited hot electrons either cause single electron desorption or they relax by equilibrating with the substrate phonons and the vibrationally excited bound states of the adsorbates which have not yet been removed by DIET. For fixed pulse fluence, qualitatively different behavior occurs depending upon the temporal width of the pulse, mainly with respect to the electron–phonon relaxation time and the energy transport or heat conduction time scale of the substrate. The crucial factor is the heating time as characterized by the pulse width in comparison with the equilibration time. If the electron–phonon relaxation time (typically many ps) is long relative to the pulse width or heating time, then an extraordinarily high electron temperature can be attained for a limited but important time duration. For systems under experimental study such as CO, NO, or O₂ on Pt, Pd, or Cu, simulations within the context of the multi-temperature model (i.e. a set of coupled heat diffusion equations governing T_{el} , T_{phonon} , and T_{ads} , the time dependent ‘temperatures’ of the initially laser-excited-electrons and the subsequently-relaxed-into phonons and/or adsorbate vibrations [22,85–91]) consistently suggest that as the pulse width decreases below a few 100 fs (~ 0.1 – 0.001 of the electron–phonon relaxation time), the maximum electron temperature attained can be several thousand K, many times in excess of the ultimate equilibrated temperatures. In contrast, for pulse widths longer than ~ 500 fs, the ultimate maximum electron temperature rise is found to be only tens or a few hundred K. Based on their numerical simulations, Newns et al. [39] have introduced the empirical functional form

$$T_{el}(t)/T_m = \mu \exp(-t/t_{relax}) / (\exp(-t/t_p) + 1) \quad (5)$$

as a computational convenience, where $\mu \equiv r(r-1)^{(1-r)/r}$ and $r = t_{relax}/t_p$. The temperature together

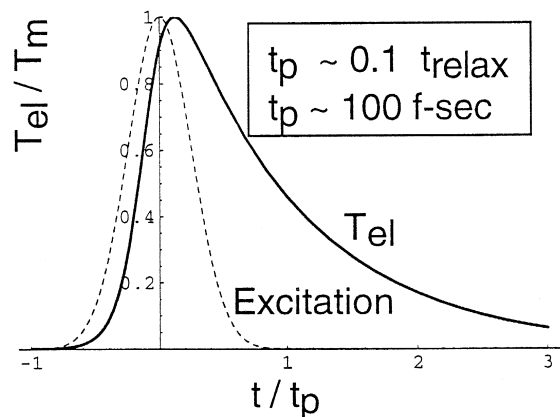


Fig. 2. Normalized electron temperature vs. time (in units of t_p , the laser excitation pulse width parameter) for an example in which t_p is of order 10% of the electron–phonon relaxation time (full curve). Also shown is the Gaussian excitation pulse (dash curve).

with the Gaussian pulse profiles are illustrated in Fig. 2 for an example in which $t_p = 0.1 t_{relax}$, as seems to be characteristic of DIMET experiments. The simulation-inspired-guidelines suggest that when $t_p \sim 100$ fs, $T_m \approx 5000$ K, at least for pulses with fluences in the range of millijoules per cm² which are typically employed in the experiments.

2.3. Thermal electron flux

A frequently used textbook exercise in statistical mechanics and solid state physics is the calculation of the uni-directional flux of thermally excited electrons with ‘normal energy’ in excess of some specified minimum $\equiv \varepsilon_{act}$. For a free electron Sommerfeld metal, the current is given as:

$$j(T_{el}) = (2e\hbar/m) \int_{\varepsilon_z > \varepsilon_{act}}^{\infty} \frac{d^3k}{(2\pi)^3} k_z f(\varepsilon(k); T_{el}) \quad (6)$$

where $f(\varepsilon; T_{el})$ is the Fermi–Dirac distribution, $\varepsilon_z = \hbar^2 k_z^2 / 2m$, and the multiplicative factor of 2 accounts for spin degeneracy. When $\varepsilon_{act} \gg k_B T_{el}$, f can be replaced by a Maxwellian $f \approx \exp(-\varepsilon/k_B T_{el})$ in which case Eq. (6) easily integrates to [66]:

$$j(T_{el}) = A T_{el}^2 \exp(-\varepsilon_{act}/k_B T_{el}) \quad (7)$$

where $A = (emk_B^2)/(2\hbar^3\pi^2) = 120 \text{ amps/cm}^2/\text{K}^2$ and $k_B = (1/11,600)\text{eV/K}$. A most common realization of Eq. (7) sets $\varepsilon_{\text{act}} = \phi$, the workfunction of the solid, in which case Eq. (7) is referred to as the Richardson–Dushman equation for thermionic electron emission.

Considering Eq. (1) or Eq. (3), it seems quite reasonable to expect that this thermal flux of laser-excited-hot electrons incident upon the surface in a DIET (or DIMET) event should also be specified by Eq. (7) when ε_{act} is defined appropriately. For instance, if a single inelastic scattering can induce desorption, then ε_{act} must be greater than D . Looking somewhat ahead, it might be anticipated that multiple scattering desorption permits a lower energy transfer per event. With this in mind it is informative to consider the numerical implications of Eq. (7), particularly when given in units that are immediately obvious on an atomic time and distance scale ($1.6 \times 10^9 \text{ amp/cm}^2 \Leftrightarrow 1 \text{ electron/ps}/\text{\AA}^2$). Letting $\varepsilon_{\text{act}} = D_n \equiv D/n$, the corresponding electron number flux $= j_n(T_{\text{el}})$ vs. T_{el} obtained from Eq. (7) is shown for several values of D_n in Fig. 3a. It is interesting (and important!) to note that even for the highest electron temperatures, the incidence of ‘energetically relevant’ electrons per atomic site per pulse (or vibrational lifetime) is much lower than would seem to be demanded by conventional DIMET or friction models. We will return to this observation shortly. The time dependence for the electron flux using the temperature–time connection given by Eq. (5) is also shown in Fig. 3b.

When considering inelastic electron scattering rather than thermionic electron emission, one must include not only the thermal occupation of initial states, but also the thermally dependent vacancy of final lower energy states into which the electrons are scattered. This is compactly dealt with within the ‘bosonized electron gas’ model in which electrons and holes obeying Fermi statistics are treated as composite boson electron–hole pairs [99–102]. The resulting pair-flux is obtained from expressions similar to Eq. (6) where an additional factor of $(1 - f(\varepsilon - D_n; T_{\text{el}}))$ appears within the integral. Ultimately this leads to the natural appearance of Bose–Einstein rather than Fermi–Dirac distribution functions. To the extent that the Maxwellian replacement is valid in Eq. (6), the same replacement in the bosonized

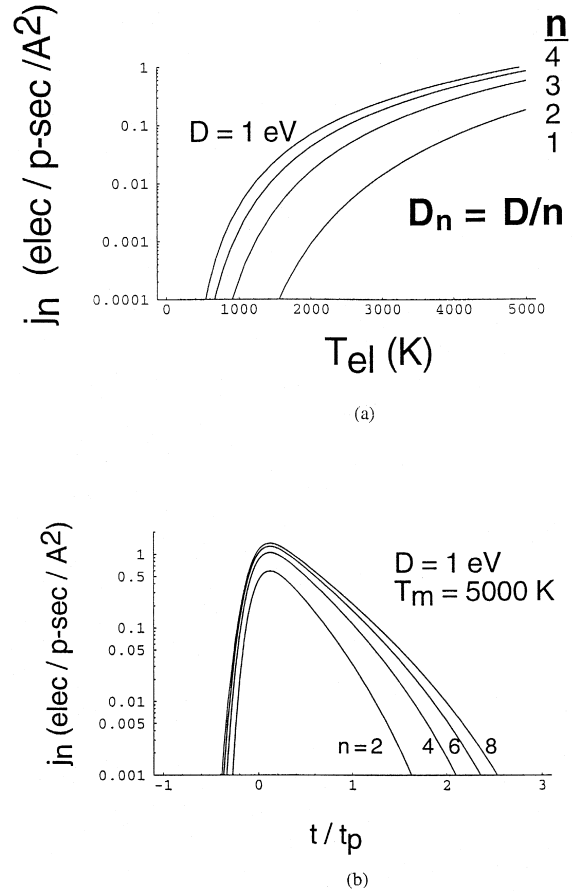


Fig. 3. (a) Hot electron flux vs. electron temperature for electron energies in excess of $D_n = D/n$, with $D = 1 \text{ eV}$ and $n = 1-4$, as labeled. (b) Hot electron flux vs. time for various D_n with $n = 2-8$, as labeled. T_{el} and t are related as shown in Fig. 2 [Eq. (5)] with $T_m = 5000 \text{ K}$.

electron gas should be adequate for present purposes, in which case the fluxes given by Eq. (7) and shown in Fig. 3 can be used. Refinements to this reduction are currently under study and will be reported in the future.

3. Multiple excitation processes

It is an obvious matter of energy conservation that *when a bond whose energy is D is broken by the energy transfer occurring through n inelastic hot electron scatterings, then on average only $\Delta\varepsilon = D_n = D/n$ must be transferred in each collision.* For

expository simplicity we will adopt a model in which the n -fold breaking of the bond follows from n events each with energy transfer $= D_n$. For a given electron temperature, the incident flux of energetically useful electrons increases with increasing n (i.e. $j_n(T_{\text{el}}) = AT_{\text{el}}^2 \exp(-D/nk_B T_{\text{el}})$), as already demonstrated in Fig. 3. On the other hand since the probability per encounter for energy transfer to occur is necessarily less than unity, the total probability for a successful n 'th order process must approach zero for 'large' n . Due to the opposing n -dependencies, an optimal multiplicity for DIMET is suggested by this proposition. This will be the central issue for the remainder of this note.

A characteristic feature of the transient dynamics occurring in fs laser induced desorption (in which $T_m > 10^3$ K) is that, since the massive electron temperature rise and fall occurs in the sub-ps time interval after the pulse, the dominant hot-electron-induced desorption will also occur within this interval. Consequently the transient desorption rate is similar to a first-passage-time climb up the vibrational ladder [92–95] associated with the adsorption bonds [96–98], a trip which, if it is to occur with significant probability, must be completed before the hot electrons equilibrate with the lattice. From this perspective, the vibrational level which is $\sim D_n$ below the desorption continuum can be regarded as the bottleneck state in the rate equation, Eq. (4). This is the highest occupied bound state prior to the final collision in which $\Delta \varepsilon \geq D_n$ is transferred into the bond. Thus the n 'th order desorption rate can be written as:

$$R_n(t) = p_{n-1} \Gamma_{n-1 \rightarrow n} \quad (8)$$

where p_{n-1} is the probability that the highest bound state (the bottleneck) is occupied and $\Gamma_{n-1 \rightarrow n}$ is the excitation rate out of the highest bound state (to the equivalent desorptive state). In the appropriate limits, Eq. (8) is similar to some of the findings of Gao, Ho, and coworkers, [4,49–51,75–77,82].

Let p be the probability per encounter that $\Delta \varepsilon_n = D/n$ is pumped into the bond ladder. Of course a proper n - and thus $\Delta \varepsilon_n$ -dependence for p must be included in a complete desorption theory, thus requiring a quantitative specification of the system-specific energy diagrams for the resonant inelastic hot electron scattering process shown in Fig. 1. Since this goes beyond the scope of the present study, we

will for now take p to be independent of n [35,36] with the realization that this should be a target for future work. With this in mind, the probability that the bottleneck state is excited after $n-1$ scattering events is then $p_{n-1} \approx p^{n-1}$, assuming that energy placed in the bond remains there, at least on the first-passage time scale. In the spirit of this model, the rate for excitation out of the bottleneck which follows from Eq. (3) is $\Gamma_{n-1 \rightarrow n}(t) \approx j_n(t) \langle \sigma_{\text{el}} \rangle p$. Eq. (8) then yields the n 'th order desorption rate within the first passage time domain,

$$R_n(t) \equiv \langle \sigma_{\text{el}} \rangle p^n j_n(t) \quad (9)$$

which, with one further refinement, demonstrates the main point of this preliminary study.

Due to the possible decay of vibrationally excited states of the adsorption bond, it is desirable to incorporate a survival probability into the sequential excitation of the bottleneck state. If τ_d is the vibrational decay time (necessarily many multiples of the relevant vibrational period which, for a mode with $\hbar \omega \approx 0.05$ eV, is $T_{\text{vibe}} \approx 0.1$ ps), then the probability for excitation survival from one electron scattering to the next is $P_{\text{surv}}(\Delta t_n) \approx \exp(-\Delta t_n/\tau_d)$, where Δt_n

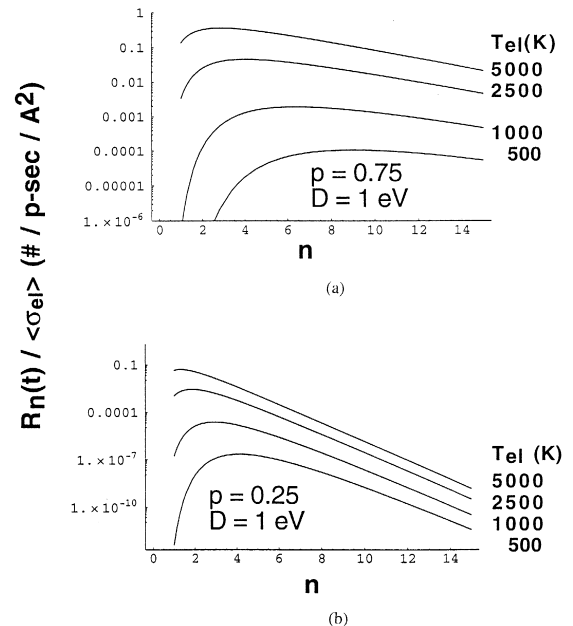


Fig. 4. Partial desorption rates as a function of n , the multiplicity, from Eq. (9), with $D = 1$ eV and a range of electron temperatures, as labeled. The excitation probability per scattering is: (a) $p = 0.75$ and (b) $p = 0.25$.

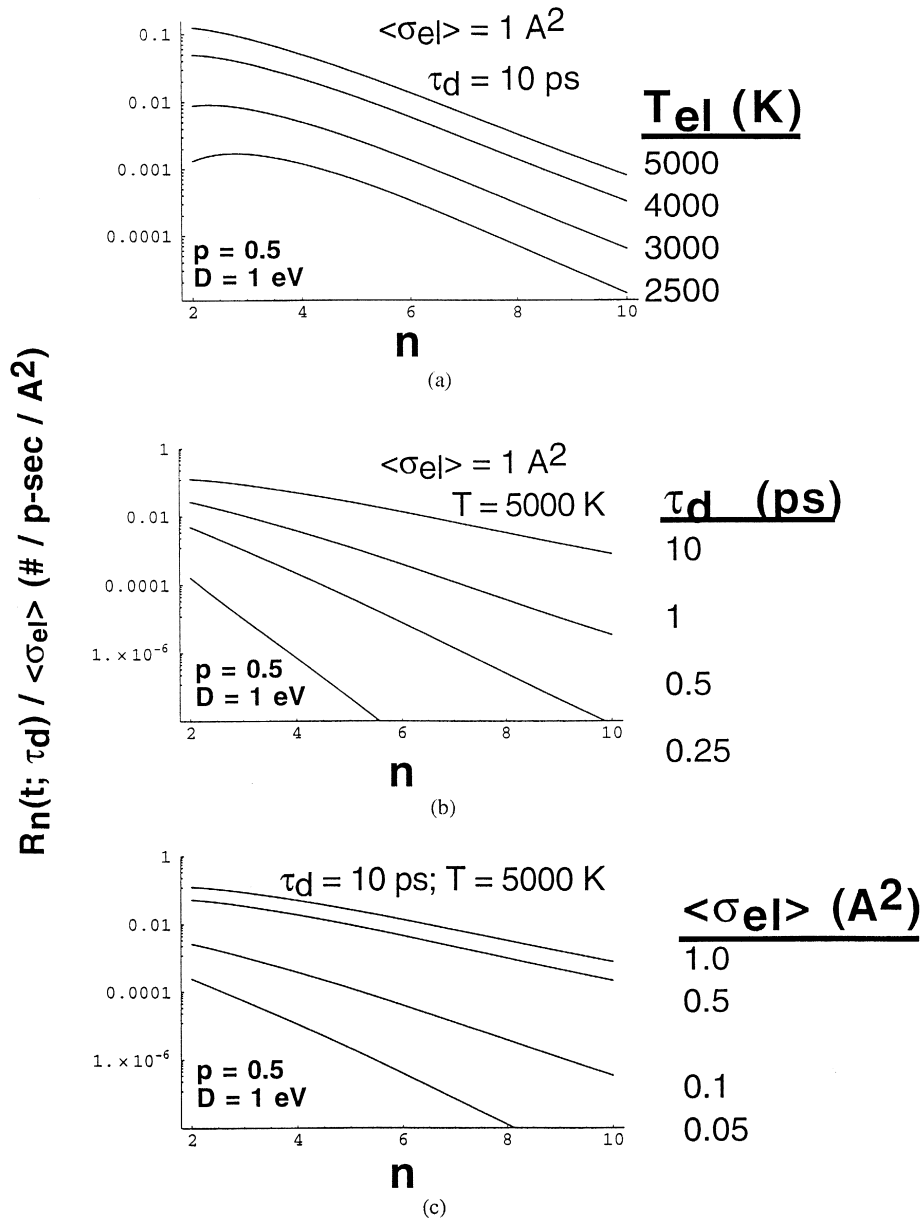


Fig. 5. Partial desorption rates as a function of n , including the effects of vibrational decay, from Eq. (10), with $D = 1$ eV and $p = 0.5$, for a range of: (a) electron temperatures, (b) vibrational decay times, and (c) capture cross sections, as labeled.

$\approx (\langle \sigma_{el} \rangle j_n)^{-1}$ is the average time between collisions. The total survival probability for an n 'th order event would thus be $P_{\text{surv}}(n, \tau_d) = (P_{\text{surv}}(\Delta t_n))^{n-1}$ and the first passage desorption rate including vibrational damping is

$$R_n(t; \tau_d) = R_n(t) P_{\text{surv}}(n, \tau_d) \quad (10)$$

which will be returned to in Section 4. The dynamic picture of the desorption process that has emerged within this framework of few- n processes is one in which excitation does proceed step-by-step up a vibrational ladder (by increments $\sim \Delta \epsilon_n = D/n$). However those paths involving extra (time consuming!) cancelling steps up and down are so much less

likely (due to the cooling of the hot electrons throughout the multiple-step process) than the direct path that they can be neglected here.

4. Results

The major aim of this study is a demonstration of the propensity (or lack thereof) for multiple-electron-scattering-induced desorption as the availability of ‘energetically relevant electrons’ is enhanced. For multiple processes this is brought about by lowering the minimum energy required per collision. The degree to which this expectation is realized is shown in Fig. 4a and b, where the n ’th order desorption rate which follows from Eqs. (7) and (9) (or 10 with $\tau_d > \Delta t_n$ so that $P_{\text{surv}}(n, \tau_d) \approx 1$) with $D = 1$ eV is shown as a function of n , for a range of electron temperatures occurring in the fs laser desorption experiments. Of course the fastest rate is associated with the highest temperature, hence the highest incident flux of hot electrons, as shown in Fig. 3. What is more revealing is the n -dependence. For a high value of $p = 0.75$, the calculated decline of R_n , after achieving a maximum at some relatively low $n \leq 10$, while not dramatic, is still very real. With a more realistic choice of $p = 0.25$, the drop of R_n , after peaking at $n \leq 4$, is much more pronounced. It is indeed hard to imagine how multiple scattering processes requiring $n \gg 10$ could be possible to any significant extent. Note that the estimates for values of p are based on the results from microscopic resonance scattering models (descriptively referred to as the ‘jumping wave packet and weighted average procedure’ by Saalfrank [44–47]) in which the probability for a specified range of hot-electron-to-adsorption-bond energy transfers per electron capture event are calculated within plausible scattering scenarios. The results presented in Fig. 6 of Ref. [35] and Fig. 6 of Ref. [37], with $D_n = D/n$ substituted for D , have provided the basis for the present choices of suggested numerical p -values.

Matters become even more dramatic when the role of vibrational damping, as embodied in the survival probability, are included. The desorption rate (including the effect of damping) calculated from Eq. (10) is shown as a function of n in Fig. 5 for a range of vibrational decay times, capture cross

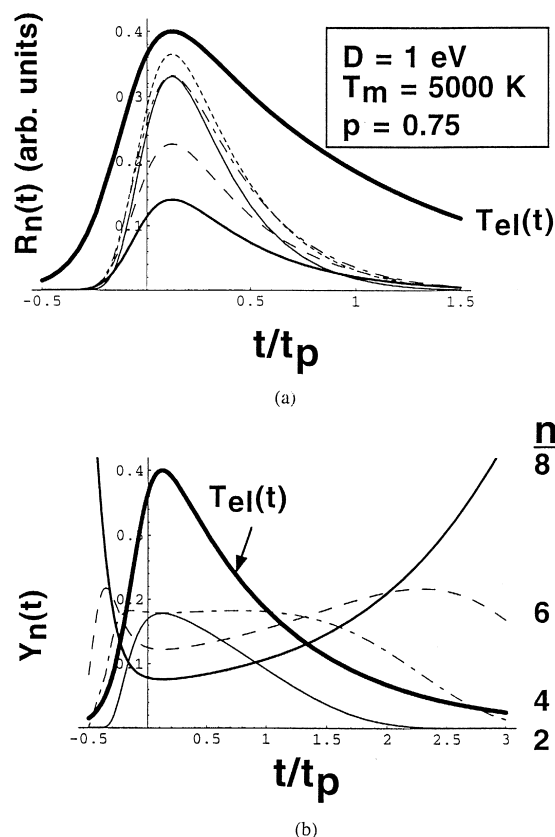


Fig. 6. (a) Partial desorption rate vs. time, with $D = 1$ eV, $T_m = 5000$ K, and $p = 0.75$. The thickest full curve is proportional to $T_{el}(t)$. The curve legends are given in decreasing order of their maximum value, realized near $t/t_p \approx 0.1$: $n = 3$ (short dash); $n = 4$ (dot-dash); $n = 2$ (thinnest full); $n = 6$ (long dash); $n = 8$ (middle full). (b) Partial desorption rate branching ratio vs. time for same system as in (a).

sections, and electron temperatures, as labeled. The global feature brought into play by the less-than-unity-survival probability is the further de-emphasis of higher n -processes, again in conflict with the DIMET and friction model requirements.

Another interesting aspect of laser excited hot-electron-induced desorption concerns the temporal evolution of the multiplicity throughout the history of a given pulse. An illustrative example is shown in Fig. 6. The electron temperature profile from Eq. (5) (with $T_m = 5000$ K, $r = 10$) and some partial desorption rates, from Eqs. (5), (7) and (9) are shown as a function of time in Fig. 6a. The point to be made

here is that the partial rate curves cross and intermingle throughout the life of the pulse such that the most favored degree of multiplicity is continuously changing. This is shown in Fig. 6b in the form of partial desorption rate branching ratios ($Y_n(t) = R_n(t)/\sum_n R_n(t)$) as a function of time. Clearly the relative roles of the possible multiplicities change throughout the process, making the assignment of a single multiplicity number a somewhat ill-defined exercise.

5. Summary

The process of hot-electron-induced desorption from a fs-laser-excited metal surface has been under study here. The particular issue of emphasis has been understanding the conditions determining the degree of multiple electron scattering which is responsible for desorption. The standard two-temperature model [22,85–91] describing the temporal evolution of the hot electron distribution has been used here as a working model. Although such a hypothesis has been extensively used [8,9,22,39,48–51,86–91], limitations on its accuracy are known to exist [103,104], see also Ref. [22], p. 327. Characterization of the hot electron relaxation would appear to be a useful area for future inquiry.

It was then noted that in a multiple-step process for overcoming an activation barrier (= desorption energy), there is often a rate-limiting final bottleneck state from which the bond-breaking/desorption occurs. In this limit the rate is simply the product of the probability that the bottleneck state is occupied (due to multiple collisions) multiplied by the rate out of the bottleneck and this is given by the single scattering rate, which in turn is a product of an electron-temperature-dependent incident flux of hot electrons multiplied by a capture cross section and by p , the probability per collision for the requisite amount of energy transfer to occur. The n 'th order rate takes the form $R_n(t) \sim p^n j_n(T_{\text{el}}(t))$ where $j_n(T_{\text{el}}(t))$, the incident flux of hot electrons with energy $\geq D/n$, is given by an expression akin to the Richardson–Dushman equation for thermionic electron emission.

The numerical implications of this study were somewhat surprising in the light of existing DIMET and stochastic friction model wisdom. First, the inci-

dent thermionic hot electron fluxes seem to be quite a bit lower than implied by the DIMET and friction models. Furthermore, ‘few- n processes’, where $1 \leq n \leq 5$ appear to be much more important (dominant?) than in the IBM-DIMET/friction scenarios, in agreement with expectations of Saalfrank and Kosloff. While the quantitative aspects of the bottleneck-limited rate theory in which so many of the energy-dependent quantities, such as the cross sections and probabilities have been dealt with in a very cavalier manner, the bottom-line observation that ‘few- n processes’ dominate, at least within the context of the 2-temperature model, seems to be robust. From this it can safely be concluded that the question ‘how multiple is multiple in fs-laser-induced DI‘M‘ET?’ is still an open question meriting further study.

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